Designation: D7876 – 13

Standard Practice for
Practice for Sample Decomposition Using Microwave Heating (With or Without Prior Ashing) for Atomic Spectroscopic Elemental Determination in Petroleum Products and Lubricants[1]

1. Scope

1.1 This practice covers the procedure for use of microwave radiation for sample decomposition prior to elemental determination by atomic spectroscopy.

1.1.1 Although this practice is based on the use of inductively coupled plasma atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS) as the primary measurement techniques, other atomic spectrometric techniques may be used if lower detection limits are required and the analytical performance criteria are achieved.

1.2 This practice is applicable to both petroleum products and lubricants such as greases, additives, lubricating oils, gasolines, and diesels.

1.3 Although not a part of Committee D02's jurisdiction, this practice is also applicable to other fossil fuel products such as coal, fly ash, coal ash, coke, and oil shale.

1.3.1 Some examples of actual use of microwave heating for elemental analysis of fossil fuel products and other materials are given in Table 1.

1.3.2 Some additional examples of ASTM methods for microwave assisted analysis in the non-fossil fuels area are included in Appendix X1.

1.4 During the sample dissolution, the samples may be decomposed with a variety of acid mixture(s). It is beyond the scope of this practice to specify appropriate acid mixtures for all possible combinations of elements present in all types of samples. But if the dissolution results in any visible insoluble material, this practice may not be applicable for the type of sample being analyzed, assuming the insoluble material contains some of the analytes of interest.

1.5 It is possible that this microwave-assisted decomposition procedure may lead to a loss of "volatile" elements such as arsenic, boron, chromium, mercury, antimony, selenium, and/or tin from the samples. Chemical species of the elements is also a concern in such dissolutions since some species may not be digested and have a different sample introduction efficiency.

1.6 A reference material or suitable NIST Standard Reference Material should be used to confirm the recovery of analytes. If these are not available, the sample should be spiked with a known concentration of analyte prior to microwave digestion.

1.7 Additional information on sample preparation procedures for elemental analysis of petroleum products and lubricants can be found in Practice D7455.

1.8 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.9 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific warning statements are given in Sections 6 and 7.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C1234 Practice for Preparation of Oils and Oily Waste Samples by High-Pressure, High-Temperature Digestion for Trace Element Determinations

C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis

C1463 Practices for Dissolving Glass Containing Radioactive and Mixed Waste for Chemical and Radiochemical Analysis

D482 Test Method for Ash from Petroleum Products

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[1] This practice is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

TABLE 1 Referenced Examples of Microwave Heating for Dissolution of Fossil Fuel and other Samples

Material	Element(s) Determined	Measurement Technique	Reference[A]
Biological Materials	Multiple	AAS and NAA	Abu Samra et al **(1)**
Biological Materials	Multiple	AAS and NAA	Barrett et al **(2)**
			West et al **(3)**
Geological Materials	Multiple		Matthes et al **(4)**
Oil Shales	Multiple	ICP-AES	Nadkarni **(5)**
Coal and Fly Ash	Multiple	ICP-AES	Nadkarni **(5)**
Plant and Grain Standards	Multiple	ICP-MS	Feng et al **(6)**
Greases	Multiple	ICP-AES	Fox **(7)**; Nadkarni **(8)**
Petroleum Products	Multiple	ICP-AES	Hwang et al **(9)**
Crude Oil	Multiple	ICP-MS	Xie et al **(10)**
Residual Fuel Oil	Multiple	ICP-MS	Wondimu et al **(11)**
Oils	Lanthanides and Platinum Group Metals	ICP-MS	Woodland et al **(12)**
		AAS; ICP-AES	Kingston and Jassie **(13)**
		AAS; ICP-AES	Kingston and Haswell **(14)**
Soils and Sediments	Lanthanides	ICP-MS	Ivanova et al **(15)**

[A] The boldface numbers in parentheses refer to the list of references at the end of this standard.

D874 Test Method for Sulfated Ash from Lubricating Oils and Additives

D1193 Specification for Reagent Water

D1506 Test Methods for Carbon Black—Ash Content

D2216 Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D4309 Practice for Sample Digestion Using Closed Vessel Microwave Heating Technique for the Determination of Total Metals in Water

D4628 Test Method for Analysis of Barium, Calcium, Magnesium, and Zinc in Unused Lubricating Oils by Atomic Absorption Spectrometry

D4643 Test Method for Determination of Water (Moisture) Content of Soil by Microwave Oven Heating

D4951 Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry

D5185 Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

D5258 Practice for Acid-Extraction of Elements from Sediments Using Closed Vessel Microwave Heating

D5513 Practice for Microwave Digestion of Industrial Furnace Feedstreams and Waste for Trace Element Analysis

D5765 Practice for Solvent Extraction of Total Petroleum Hydrocarbons from Soils and Sediments Using Closed Vessel Microwave Heating

D5862 Test Method for Evaluation of Engine Oils in Two-Stroke Cycle Turbo-Supercharged 6V92TA Diesel Engine (Withdrawn 2009)[3]

D6010 Practice for Closed Vessel Microwave Solvent Extraction of Organic Compounds from Solid Matrices

D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories

D7260 Practice for Optimization, Calibration, and Validation of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for Elemental Analysis of Petroleum Products and Lubricants

D7303 Test Method for Determination of Metals in Lubricating Greases by Inductively Coupled Plasma Atomic Emission Spectrometry

D7455 Practice for Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis

D7740 Practice for Optimization, Calibration, and Validation of Atomic Absorption Spectrometry for Metal Analysis of Petroleum Products and Lubricants

E1358 Test Method for Determination of Moisture Content of Particulate Wood Fuels Using a Microwave Oven

E1645 Practice for Preparation of Dried Paint Samples by Hotplate or Microwave Digestion for Subsequent Lead Analysis

2.2 *Other documents:*

CFR 1030.10 Radiological Health

FCC Rule Part 18 Labelling Guidelines, Labelling, Information to User, Information in Manual, User Manual

3. Terminology

3.1 *Definitions:*

3.1.1 *AAS, n*—atomic absorption spectrometry, an analytical technique for measuring metal content of solutions, based on a combination of flame source, hollow cathode lamp, photomultiplier, and a readout device. **D7740**

3.1.2 *additive, n*—a material added to another, usually in small quantities, to impart or enhance desirable properties or to suppress undesirable properties. **D5862**

3.1.3 *blank, n*—solution which is similar in composition and contents to the sample solution but does not contain the analyte being measured. **D7740**

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[3] The last approved version of this historical standard is referenced on www.astm.org.

3.1.4 *certified reference material, n*—a reference material one or more of whose property values are certified by a technically valid procedure, accompanied by a traceable certificate or other documentation which is issued by a certifying body. **D6792**

3.1.5 *dilution factor, n*—ratio of the sample weight of the aliquot taken to the final diluted volume of the solution.

3.1.5.1 *Discussion*—The dilution factor is used to multiply the observed reading and obtain the actual concentration of the analyte in the original sample. **D7740**

3.1.6 *ICP-AES, n*—inductively coupled plasma atomic emission spectrometry, a high temperature discharge generated by passing an ionizable gas through a magnetic field induced by a radio frequency coil surrounding the tubes that carry gas. The light emitted by excited atoms by this process is measured at fixed wavelengths specific to elements of interest and converted to their concentrations in a sample.

3.1.7 *reference material (RM), n*—a material with accepted reference value(s), accompanied by an uncertainty at a stated level of confidence for desired properties, which may be used for calibration or quality control purposes in the laboratory.

3.1.7.1 *Discussion*—Sometimes these may be prepared "in-house" provided the reference values are established using accepted standard procedures. **D6792**

3.1.8 *standard reference material (SRM), n*—trademark for reference materials certified by National Institute of Standards and Technology. **D7740**

4. Summary of Practice

4.1 A weighed portion of the sample is subjected to alternate means of sample dissolution which may include (optional) sulfated ashing in a muffle furnace followed by closed or open vessel microwave digestion in acid(s). Ultimately, these diluted acid solutions are analyzed using AAS or ICP-AES. By comparing absorbance or emission intensities of elements in the test specimen with those measured of the calibration standards, the concentrations of elements in the test specimen can be calculated.

4.1.1 The final elemental determinations can also be done using ICP-MS; cold vapor and hydride generation AFS/AAS can be used for mercury and hydride forming elements; however, there is no standard ASTM procedure for such work at present.

4.2 Optimal conditions for microwave digestion depend on sample weight, composition, volume of digestion acid reagents, and the microwave system used.

5. Significance and Use

5.1 Often it is necessary to dissolve the sample, particularly if it is a solid, before atomic spectroscopic measurements. It is advantageous to use a microwave oven for dissolution of such samples since it is a far more rapid way of dissolving the samples instead of using the traditional procedures of dissolving the samples in acid solutions using a pressure decomposition vessel, or other means.

5.2 The advantage of microwave dissolution includes faster digestion that results from the high temperature and pressure attained inside the sealed containers. The use of closed vessels also makes it possible to eliminate uncontrolled trace element losses of volatile species that are present in a sample or that are formed during sample dissolution. Volatile elements arsenic, boron, chromium, mercury, antimony, selenium, and tin may be lost with some open vessel acid dissolution procedures. Another advantage of microwave aided dissolution is to have better control of potential contamination in blank as compared to open vessel procedures. This is due to less contamination from laboratory environment, unclean containers, and smaller quantity of reagents used (**9**).

5.3 Because of the differences among various makes and models of satisfactory devices, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular device.

5.4 *Mechanism of Microwave Heating*—Microwaves have the capability to heat one material much more rapidly than another since materials vary greatly in their ability to absorb microwaves depending upon their polarities. Microwave oven is acting as a source of intense energy to rapidly heat the sample. However, a chemical reaction is still necessary to complete the dissolution of the sample into acid mixtures. Microwave heating is internal as well as external as opposed to the conventional heating which is only external. Better contact between the sample particles and the acids is the key to rapid dissolution. Thus, heavy nonporous materials such as fuel oils or coke are not as efficiently dissolved by microwave heating. Local internal heating taking place on individual particles can result in the rupture of the particles, thus exposing a fresh surface to the reagent contact. Heated dielectric liquids (water/acid) in contact with the dielectric particles generate heat orders of magnitude above the surface of a particle. This can create large thermal convection currents which can agitate and sweep away the stagnant surface layers of dissolved solution and thus, expose fresh surface to fresh solution. Simple microwave heating alone, however, will not break the chemical bonds, since the proton energy is less than the strength of the chemical bond (**5**).

5.4.1 In the electromagnetic irradiation zone, the combination of the acid solution and the electromagnetic radiation results in near complete dissolution of the inorganic constituents in the carbonaceous solids. Evidently, the electromagnetic energy promotes the reaction of the acid with the inorganic constituents thereby facilitating the dissolution of these constituents without destroying any of the carbonaceous material. It is believed that the electromagnetic radiation serves as a source of intense energy which rapidly heats the acid solution and the internal as well as the external portions of the individual particles in the slurry. This rapid and intense internal heating either facilitates the diffusion processes of the inorganic constituents in solution or ruptures the individual particles thereby exposing additional inorganic constituents to the reactive acid. The heat generated in the aqueous liquid itself will vary at different points around the liquid-solid interface and this may create large thermal convection currents which can agitate and sweep away the spent acid solution containing

TABLE 2 Suggested Wavelengths for Some Elements Determined after Sample Digestion

Element	AAS Wavelength, nm	ICP-AES Wavelength, nm
Aluminum	393.1, 309.27	167.038, 308.22, 396.15, 309.27
Antimony	217.58	206.83, 217.58, 231.15
Barium	553.6	223.53, 233.527, 455.40, 493.41
Boron	249.77	249.77, 208.96
Calcium	422.67	315.88, 317.93, 364.4, 396.85, 422.67
Chromium	357.87	267.72, 357.87
Copper	324.75	324.75, 327.40
Iron	248.3, 372.0	238.20, 259.94
Lithium	670.78	670.78, 610.36, 460.29
Magnesium	285.2	279.08, 279.55, 280.278, 285.21
Manganese	279.2	257.61, 293.31
Molybdenum	313.3	135.387, 202.03, 281.62
Nickel	232.0, 341.48	231.60, 341.48
Phosphorus	- -	177.51, 178.29, 213.62, 214.91, 253.40
Potassium	766.49	766.49, 404.72
Silicon	251.618	288.16, 251.618
Sodium	589.595	589.595
Vanadium	318.4	292.40, 290.88
Zinc	213.86, 398.8	202.55, 206.20, 213.86, 334.58, 481.05

dissolved inorganic constituents from the surface layers of the carbonaceous particles thus exposing the particle surfaces to fresh acid (**16**).

5.4.2 Unlike other heating mechanisms, true control of microwave heating is possible because stopping of the application of energy instantly halts the heating (except the exotherms which can be rapid when pure compounds are digested). The direction of heat flow is reversed from conventional heating, as microwave energy is absorbed by the contents of the container, energy is converted to heat, and the bulk temperature of the contents rises. Heat is transferred from the reagent and sample mixture to the container and dissipated through conduction to the surrounding atmosphere. Newer synthesized containers made up of light yet strong polymers can withstand over 240°C temperatures and over 800 psi pressure. During the digestion process of samples containing organic compounds, largely insoluble gases such as CO_2 are formed. These gases combine with the vapor pressure from the reagents, at any temperature, to produce the total pressure inside the vessel. Since the heat flow from a microwave digestion vessel is reversed from that of resistive devices, the total pressures generated for microwave dissolutions are significantly lower at the same temperature than other comparably heated devices or systems. This means larger samples can be digested at higher temperatures and lower pressures than would normally be expected from such pressurized vessels. Sample size should be controlled to prevent rapid exotherm rupture, exacerbated by excess CO_2 generation. However, the pressure limitations of the vessel still restrict both the sample size that can be used and the maximum temperature that can be achieved due to the vapor pressure resulting from the reagents (**17**).

5.4.3 Organic and polymer samples can be especially problematic because they are highly volatile and produce large amounts of gaseous by-products such as CO_2 and NO_x. As a result larger sample sizes will produce higher pressures inside the digestion vessel. Generally, no more than 1 g of these sample types can be digested in a closed vessel (**18**).

5.4.3.1 While in open digestion vessel systems the operating temperatures are limited by the acid solutions' boiling points, temperatures in the 200–260°C range can be typically achieved in sealed digestion vessels. This results in a dramatic acceleration of the reaction kinetics, allowing the digestion reactions to be carried out in a shorter time period. The higher temperatures, however, result in a pressure increase in the vessel and thus in a potential safety hazard. Rapid heating of the sample solution can induce exothermic reactions during the digestion process. Therefore in modern microwave digestion systems, sensors and interlocks for temperature and pressure control are introduced. Since different types of sample behave differently in microwave field, heating control is necessary in this operation (**19**).

5.4.4 Microwave heating occurs because microwave reactors generate an electromagnetic field that interacts with polarizable molecules or ions in the materials. As the polarized species compete to align their dipoles with the oscillating field, they rotate, migrate, and rub against each other, causing them to heat up. This microwave effect differs from indirect heating by conduction achieved by using a hot plate (**20**).

6. Apparatus

6.1 *Analytical Balance,* capable of weighing to 0.001 g or 0.0001 g, capacity of 150 g.

6.2 *Atomic Absorption Spectrometer,* with appropriate hollow cathode lamps for analytes of interest, readout, and so forth.

6.3 *Inductively Coupled Plasma Atomic Emission Spectrometer*—Either a sequential or simultaneous spectrometer is suitable, if equipped with a quartz ICP torch and RF generator to form and sustain the plasma. Suggested wavelengths for the determinations of elements in dissolved acid solutions are given in Table 2. These wavelengths are only suggested and do not represent all possible choices. Wavelengths for boron, phosphorus, and sulfur below 190 nm require that a vacuum or inert gas purge optical path be used in ICP-AES instrument.

6.4 *Microwave Oven,* commercially available laboratory microwave digestion oven of sufficient power is suitable. The units should be capable of 1 % power adjustment and 1 s time adjustment. The oven cavity should be fluorocarbon- coated or coated with a material that has equivalent acid resistance and microwave properties and be equipped with exhaust ventilation at 2.8 m^3/min (100 ft^3/min) for acid vapor protection of the unit and operator. The unit must have a rotating or alternating turntable, capable of holding multiple digestion vessels, to ensure even sample heating. Safety interlocks, to shut off magnetron power output, must be contained in the oven door opening mechanism. The unit may contain a temperature control device capable of controlling vessel pressure to a minimum of 100 psig.

6.4.1 The unit must comply with U. S. Health and Human Services Standards under CFR Part 1030.10, sub parts (C) (1), (C) (2), and (C) (3), for microwave leakage. The unit should have FCC-type approval for operations under FCC Rule Part 18.

6.5 *Sample Digestion system with Closed Vessel,* quartz or polytetrafluoroethylene (PTFE) digestion vessels capable of holding 100 mL of solution. The vessel must be transparent to microwave energy and capable of withstanding internal pressures of 100 psig and temperatures of 200°C generated from the digestion of 0.2 g of sample. (Pressure achieved with a 100 mL vessel and 0.2 g of sample could be in excess of 100 psi).The vessel must contain a safety pressure relief valve, rupture disc, pressure venting system or be connected to an external safety relief valve that will prevent possible vessel rupture or ejection of the vessel cap. Microwave digestion systems with temperature and pressure monitoring devices are recommended for safety of personnel and accuracy of sample preparation.

6.5.1 The closed vessel should be operated in accordance with the manufacturer's recommended operating and safety instructions.

NOTE 1—Follow the manufacturer's suggested vessel cleaning instructions to avoid possible sample contamination.

6.5.2 The microwave digestion dishes are also commercially available. (**Warning—**Take all necessary precautions to prevent exposure to radiofrequency (RF) radiation. See Sections 6 and 9 for specifics.)

6.6 For cleaning the microwave vessels follow the manufacturer's recommended cleaning procedure. Commonly, soak the fluoropolymer vessel parts in cleaning solution (1:1 mixture of nitric acid and water) at 60°C for 10 min. Other suitable cleaning reagents may be used if appropriate. Remove the vessel parts from the cleaning solution and thoroughly rinse the parts with tap water and then with reagent water. Allow the vessel parts to air-dry or wipe dry using a clean, soft cloth.

6.7 The sample digestion system requires essentially microwave transparent and reagent resistant suitably inert polymeric materials (examples are PFA or TFM) to contain acids and samples. For higher pressure capabilities, the vessel may be contained within layers of different microwave transparent materials for strength, durability, and safety. The vessels internal volume should be at least 45 mL, capable of withstanding pressures of at least 30 atm (30 bar or 435 psi), and capable of controlled pressure relief. These specifications are given to provide an appropriate, safe, and durable reaction vessel of which there are many adequate designs by many commercial suppliers.

6.8 *Rotating Turntable,* to ensure homogenous distribution of microwave radiation within most systems. The speed of the turntable should be a minimum of 3 r/min. (**Warning—**It is not recommended to place a microwave unit in a fume hood, where it is surrounded by acid fumes, which can cause corrosion of the equipment. Acid fumes generated inside the oven cavity should be air swept away from the oven cavity to a hood.)

6.9 *Combustion Dishes,* Vycor, quartz, or platinum evaporation dishes of 250 mL size.

6.10 *Volumetric Flasks,* polypropylene or similar materials of 25, 50, or 100 mL sizes.

6.11 *Electric Muffle Furnace,* capable of maintaining 525 ± 25°C and sufficiently large to accommodate several 250 mL Vycor beakers. The capacity of an air bleed is advantageous and optional. (**Warning—**Take all necessary precautions to prevent exposure to very hot surfaces.)

6.12 *Heating Lamp,* commercial infrared heating lamp.

6.13 *Specimen Solution Containers,* of appropriate size, glass or polyolefin vials or bottles, with screw caps without metal liners, to prevent trace element contamination.

7. Reagents and Materials

7.1 *Purity of Reagents*—At a minimum, reagent grade chemicals shall be used in all tests. When ICP-MS analysis is desired, the reagents should be of ultra-pure quality. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Concentrated Sulfuric, Nitric, Hydrochloric, Perchloric, and/or Hydrofluoric Acids,* as needed. (**Warning—**Causes severe burns. Corrosive.) (**Warning—**Hydrofluoric acid is poisonous and must be handled with care as it causes painful sores on the skin usually noticed on the next day only. Avoid inhaling the fumes. Liquid or vapor causes severe irritation of eyes. Skin contact causes severe burns. Wash the skin with copious amounts of water. HF should not be used in the laboratory unless there is antidote material such as calcium gluconate or other remedies are on hand.)

7.3 *Aqueous Standard Solutions,* individual aqueous elemental solution calibration standards in appropriate concentration ranges of elements of interest. These can be prepared by dissolving pure metal compounds in water or dilute acids, or may be purchased from commercial sources.

7.3.1 Multi-element aqueous standards may be advantageous to use.

7.4 *Water,* distilled or deionized, unless otherwise indicated, references to water shall be understood to mean Type II reagent grade water as defined in Specification D1193.

7.5 *Quality Control (QC) Samples,* preferably are portions of one or more sample type materials that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process.

8. Sampling

8.1 The objective of sampling is to obtain a test specimen that is representative of the entire quantity. Thus, take laboratory samples in accordance with the instructions in Practice D4057 and D4177. The specific sampling technique can affect the accuracy of eventual final measurement of elements in samples prepared per this Ppractice.

9. Analysis

9.1 *Preparation of Ash or Sulfated Ash:*

9.1.1 If petroleum product or lubricant samples need to be ashed or sulfated ashed, use Standard Test Methods D482 or D874, respectively.

9.1.2 A sample may be ashed in a controlled fashion over a Meeker burner using a Vycor or a platinum vessel.

9.1.3 Dry ashing may also be achieved by using microwave assisted dry ashing. Take approximately 1 g of sample in a Vycor crucible, raise the temperature to 525°C over a 2-h period. Hold the temperature for 1 h at that temperature. After the sample cools to room temperature, the ash can be dissolved in suitable acid.

NOTE 2—During various dry- or wet-ashing techniques there is possibility of volatilization of certain elements or compounds depending upon their volatility, and the ashing temperature used. It would be impossible to categorize all such circumstances here.

9.2 *Open-Vessel Microwave Oven Dissolution:*

9.2.1 Take approximately 1 g of sample into the digestion vessel and add about 10 mL of nitric acid. Set the microwave oven to 30 W to cause a gentle reflux of the nitric acid. After about one hour or when the sample is nearly decomposed, add perchloric acid drop-wise. (**Warning—**Perchloric acid is an extremely strong oxidizer that may react violently with organic material. Never let the perchloric acid go to dryness. Experienced personnel only should use it with utmost caution. Note that unattended operation or venting in unmonitored vessel can result in the solution going to dryness.)

NOTE 3—Optimal conditions for microwave digestion depend on sample weight, sample composition, volume of digestion reagents, and the microwave system used. Usually 0.1 g of the sample is weighed into a pre-cleaned microwave suitable PTFE digestion vessel, and appropriate volume of mineral acids are added to it before sealing the vessel and subjecting it to microwave radiation.

9.2.2 Wash the dissolved and clear content of the vessel into a 50 mL volumetric flask and bring up to volume with water.

9.3 *Closed Vessel Microwave Oven Dissolution:*

9.3.1 Accurately weigh about 0.1 to 1 g of the sample in a TFE-fluorocarbon digestion vessel with pressure relief mechanism. Add about 4 mL (or at least the minimum acid volume recommended by the instrument manufacturer) of concentrated nitric, hydrochloric, or other appropriate mineral acid. Note that sulfuric and phosphoric acids have boiling points sufficiently high to melt through some fluocopolymer vessels.

9.3.2 Set the microwave oven at 125 W for 15 min. Then ramp the oven up to 190 W for another 15 min. After the cycle is finished, place the vessel in an ice bath for at least one hour to cool. Dissolve the washed sample solution into a 25 mL volumetric flask and bring up to volume with water. An operator initiating a reaction should not cause an overpressure venting event due to disturbing hot vessels. Whether the reaction has gone to completion is dependent on the sample type heating cycle (versus the number of vessels and sample/reagent volumes, and so forth).

NOTE 4—Care must be taken to keep the internal temperature and pressure within the capability of the vessels. Excessive heat and pressure will cause the pressurized digestion vessels to deform and potentially leak or explode.

NOTE 5—From a safety viewpoint, when digesting samples containing volatile or easily oxidized organic compounds, initially weigh no more than 0.10 g and observe the reaction before capping the vessel. If a vigorous reaction occurs, allow the reaction to cease before capping the vessel. If no appreciable reaction occurs, a sample weight up to 1 g can be used.

NOTE 6—Some microwave oven models may be capable of simultaneously processing multiple sample digestion vessels.

9.3.3 Temperature control of closed vessel microwave devices provides the main feedback control performance mechanism for the method. Control requires a temperature sensor in one or more vessels during the entire decomposition. The microwave decomposition system should sense the temperature to within ±2.5°C and permit adjustment of the microwave output power within 2 s.

NOTE 7—Ensure that the control sensor is in vessel that is undergoing a similar decomposition reaction as the other vessels in the microwave.

9.3.4 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high concentration and low concentration samples, all digestion vessels (fluoropolymer liners only) should be cleaned with appropriate acid reagents (for example, by leaching with hot (1:1) hydrochloric acid (greater than 80°C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80°C, but less than boiling) for a minimum of two hours and rinsed with reagent water and dried in a clean environment. It is preferable to use the same reagent mixture that will be used to dissolve the sample as also for cleaning the vessels. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10 % V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment.

NOTE 8—The cleanliness of the laboratory is even more important as the sample size decreases. Trace contamination becomes magnified when dilution factors are large.

9.3.4.1 Alternative cleaning procedures may be utilized if they are shown to be satisfactory.

9.3.5 The analyst should be aware of the potential for a vigorous reaction (exotherms due to rapid exothermic reaction between reagents and samples). This will have effect on maximum temperature/pressure attained, inability to stop an exotherm with suspending input energy. Pure compounds offer greater potential for this problem. If a vigorous reaction occurs upon the initial addition of reagent or the sample is suspected of containing easily oxidizable materials, allow the sample to predigest in the uncapped digestion vessel. Heat may be added in this step for safety considerations (for example the rapid release of carbon dioxide from carbonates, easily oxidized organic matter, and so forth). Once the initial reaction has ceased, the sample may continue through the digestion procedure.

9.3.5.1 The maximum sample weight used on closed vessel microwave digestion systems for total organics should not be more than 1 g; less with pure organic compounds.

9.3.5.2 Sample types make significant difference to their reaction with reagents in a microwave digestion system. This may span from instant, to more moderate reaction (for example, with crude oil and nitric acid) to slow or no reaction with coke samples.

9.3.6 Seal the vessel according to the manufacturer's directions. Properly place the vessel in the microwave system according to the manufacturer's recommended specifications and connect appropriate temperature and pressure sensors to vessels according to manufacturer's specifications.

9.3.7 Pressure control for a specific matrix is applicable if instrument conditions are established using temperature control. Because each matrix will have a different reaction profile, performance using temperature control must be developed for every specific matrix type prior to use of the pressure control system. At the end of the microwave program, allow the vessels to cool for a minimum of 5 min before removing them from the microwave system.

9.3.7.1 The acids used in the dissolution procedure may attack the pressure transducer and become contaminated.

9.3.8 Different microwave systems operate at different heating and ramping rate cycles.

9.3.8.1 For some microwave ovens, program the microwave oven to heat at 125 W for 15 min, then ramp up to 190 W for another 15 min.

9.3.8.2 For devices delivering a measured power of 575 to 635 W, program the instrument time for 50 min and the power to 100 %. For devices with a measured power of 635 to 700 W, program the instrument time for 30 min and the power for 100 %. These heating parameters will allow the samples to reach a maximum temperature of 164 ± 4°C. For some sample types it may be necessary to reach 180°C or higher for proper dissolution and satisfactorily recover many of the elements of interest. Instruments delivering greater than 700 W must be operated at reduced powers such that the sample heating rates match the heating rate suggested by the manufacturer. Depress the start key and allow the sample mixtures to heat for the programmed time.

NOTE 9—Different microwave oven models may require different temperature ramping and holding profiles based on the exact requirements of decomposition.

9.3.8.3 Every vessel being monitored for temperature and pressure, still will not stop an overpressure due to an exotherm.

9.3.9 If a turntable is used in the microwave oven device for uniform distribution of heat, the sample dissolution containers should be placed on the turntable in a balanced fashion. If an odd number of samples is to be digested, use an extra vessel to mass balance the carousel or a reagent blank to balance the power. Manufacturer's instructions should be followed.

9.3.10 Rotate the turntable through several 360° rotations of the carousel, Check to make sure that the lines are not tangled and to preserve the integrity of the safety features.

9.3.11 Detailed safety recommendations specific to the model and manufacturer of the microwave digestion system is beyond the scope of this practice. The user of this practice is advised to consult the equipment manual, the manufacturer and other literature sources for proper safe operation of the digestion system. The user should be advised that digestion of samples within the scope of this method could rapidly generate high pressure beyond the mechanical capacity of the vessel, which may cause a rupture of the vessel and damage to the digestion system. The user of this method should exercise caution when handling vessels after they have been heated since they may posses high internal pressures. (**Warning—**The outer layers of vessels are frequently not as acid or reagent resistant as the liner material and must not be chemically degraded or physically damaged to retain the performance and safety required. Routine examination of the vessel materials may be required to ensure their safe use.) (**Warning—**Another safety concern relates to the use of sealed containers without pressure relief devices. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures, but must be safely contained. However, many digestion vessels constructed from certain suitably inert polymerics may crack, burst, or explode in the unit under certain pressures. Only suitably inert polymeric (such as PFA or TFM and others) containers with pressure relief mechanisms or containers with suitably inert polymeric liners and pressure relief mechanisms are considered acceptable. Users are therefore advised not to use domestic (kitchen) type microwave ovens or to use inappropriate sealed containers without pressure relief for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to minimize safety hazards.) (**Warning—**Laboratories should not use domestic (kitchen) type microwave ovens for this method. There are several significant safety issues. First, when an acid such as nitric is used to effect sample digestion in microwave units in sealed vessels equipment, there is the potential for the acid gas vapor released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a system with isolated and corrosion resistant safety devices prevents this from occurring.) (**Warning—**Toxic nitrogen oxide(s), hydrogen fluoride, and toxic chlorine (from the addition of hydrochloric acid) fumes are usually produced during digestion. Therefore, all steps involving open or the opening of microwave vessels must be performed in a properly operating fume ventilation system.) (**Warning—**The analyst should wear protective gloves and face protection and must not at any time permit a solution containing acid to come in contact with skin or lungs.)

9.3.12 If rupture disc fails in the pressure sensing vessel, the microwave will automatically stop, but if it fails in one of the other vessels, the microwave may or may not stop. Press the stop button and wait at least one hour before removing the vessels. Do not open the microwave oven door for at least 15 min after stopping because another disc may fail, spewing hot acid.

9.3.13 After the heating cycle is complete, (as an option if necessary) place the heating pressure vessels in an ice bath for about an hour to cool. Samples may also be cooled in a refrigerator for a sufficient length of time. Shake the vessels with caution (to prevent any rapid out-gassing of vapor or liquid causing acid burns of the exposed skin of the operator) to mix the sample solutions and vent to atmosphere any gas pressure that may be present in the vessel. There could be a potential for contamination from the melted ice on the vessel exterior (assuming that the ice is not from deionized water).

9.3.13.1 The analyst may choose to monitor the temperature and pressure, and not remove the vessels from the microwave unit until they are suitable to handle.

9.3.13.2 Some microwave pressure vessels have vent holes that prohibit their placement in ice bath without sample contamination. Some microwave heat manufacturers include a cool-down step in the digestion process to prevent users from accidently venting a highly pressurized vessel.

9.3.14 Quantitatively transfer the dissolved sample into a 25 or 50 mL volumetric flask and bring it up to volume with deionized water. Dilution may be carried out on a weight or volume basis.

9.3.15 Detach the vent tubing and remove the vessel assembly from the turntable. Weigh the cooled vessel system. If there is a weight loss of greater than 0.5 g, open the vessel and add an amount of reagent water equal to the weight loss. Liquid loss of less than 10 % has not been found to result in any analyte loss. Recap the vessel and then shake the vessel to mix the sample solution.

9.3.16 If any pressure remains in the vessels when they are opened, then hot acidic fumes or liquids may spew forth endangering the operator.

NOTE 10—Care must be exercised when opening the pressure vessel so that the contents do not spill out.

NOTE 11—There may be some insoluble residue at the end of dissolution steps above if the sample contains refractory elements such as silicon, molybdenum, barium, and so forth. In such cases use of hydrofluoric acid to dissolve the residue may be required. If HF is used, HF-resistant labware must be used during the dissolution steps. Also, an HF-resistant ICP sample introduction system should be used if silicon is to be quantified and to minimize potential damage to the "solution wetted" glass components in the ICP. If HF is used, volatile elements such as silicon may be lost as silicon hexafluoride. HF can be passivated by adding dilute boric acid to the acid solution Some post-digestion organic residue may also remain in the microwave digestion vessels and seals. They can be identified as floating immiscible organic residue or "ring" around the liquid level of the microwave digestion vessel, most likely leached of any analyte and not containing any metals.

NOTE 12—Samples containing large amounts of organics may experience excessive loss of liquid (greater than 10 %); therefore, a study may be required to determine if any analyte loss has occurred. CO_2 loss is a potential but there could be losses of other volatile analytes.

9.4 *Spectrochemical Measurements:*

9.4.1 Once the sample solution is prepared by the above procedure, the elements of interest in it can be analyzed using AAS or ICP-AES instrumentation using aqueous metal calibration standards.

9.4.2 Suggested wavelengths for AAS and ICP-AES measurements are given in Table 2. These are the most commonly used lines. However, other suitable interference-free lines may also be used.

NOTE 13—Examples of spectroscopic measurement procedures can be found in various ASTM standards such as Test Method D4628 for AAS, or Test Methods D4951 and D5185 for ICP-AES. Standard operating protocols for AAS and ICP-AES can be found in Practices D7740 and D7260, respectively.

10. Calculations

10.1 Calculate the concentration of metals in the original sample by comparing the intensity of sample solution signal multiplied by the dilution factor, and divided by the intensity of the calibrant solution.

11. Keywords

11.1 atomic absorption spectrometry; inductively coupled plasma atomic emission spectrometry; lubricants; metals determination; microwave heating; petroleum products

APPENDIX

(Nonmandatory Information)

X1. ADDITIONAL INFORMATION ON THE USE OF MICROWAVE HEATING IN ANALYSIS

X1.1 Several ASTM standards illustrate other applications of microwave heating in analysis of diverse materials.

X1.1.1 *Ash Content of Carbon Black*—Test Method D1506: A pre-dried sample of carbon black is weighed before and after combustion for 16 h in the muffle furnace or 2 to 6 h in a microwave ashing furnace at 550 ± 25°C. The remaining ash is weighed for calculating the percent ash of the dried sample.

X1.1.2 *Water Content of Soil*—Test Method D4643: This procedure outlines the method for determining the water (moisture) content of soils by incrementally drying soil in a microwave oven. This method is faster than standard Test Method D2216, but may be slightly less accurate.

X1.1.3 *Moisture Content of Particulate Wood Fuels*—Test Method E1358: This is an alternative rapid method for determining moisture of particulate wood fuels. Moisture is determined by establishing the loss in mass of the sample when heated under rigidly controlled conditions of temperature, time, sample mass, and equipment specifications. Any standard commercial microwave oven having a power output of at least 600 W can be used.

X1.1.4 *Acid Extraction of Elements from Sediments*—Practice D5258: This procedure covers the digestion of soils and sediments for subsequent determinations of certain elements by AAS or ICP-AES. The sample is digested with nitric acid in a closed fluoropolymer vessel using microwave heating to an internal pressure of 100 psi.

X1.1.5 *Solvent Extraction of Total Petroleum Hydrocarbons from Soils and Sediments*—Practice D5765: This procedure uses a closed vessel microwave heating for extraction and subsequent determination of total petroleum hydrocarbons by gravimetric or gas chromatographic techniques. The sample is extracted with acetone/hexane in a sealed microwave transparent vessel by using microwave heating to an internal temperature of 150°C.

X1.1.6 *Closed Vessel Microwave Solvent Extraction of Organic Compounds from Solid Matrices*—Practice D6010: This method is applicable to soils, sediments, sludges, and wastes for subsequent determination of solvent extractable semivolatile and nonvolatile organic compounds by such techniques such as gas chromatography and gas chromatography-mass spectrometry. A 1 to 5 g portion of a solid sample is extracted in a sealed microwave transparent extraction vessel at 115°C temperature with 30 mL of acetone-hexane (1 + 1). After extraction, the vessels are cooled to room temperature, opened, and the solvent and sample are separated by decanting, filtration, or centrifugation. This is followed by quantitative determination by GC or GC-MS.

X1.1.7 *Preparation and Dissolution of Uranium Materials for Analysis*—Practice C1347: Dissolution of uranium materials for the determination of elemental, isotopic, and impurities is achieved with nitric acid, hydrochloric acid, leaching with nitric acid and treatment of residue by carbonate fusion, carbonate fusion, or by microwave heating.

X1.1.8 *Dissolution of Glass Containing Radioactive and Mixed Wastes for Chemical and Radiochemical Analysis*—Practice C1463: The ground glass sample is dissolved using a mixture of HF and NHO. Boric acid is added to the resulting solution to complex excess fluoride ions. Later the solution is analyzed using AAS, ICP-AES, or ICP-MS.

X1.1.9 *Sample Digestion Using Closed Vessel Microwave Heating Technique for the Determination of Total Metals in Water*—Practice D4309: This practice is applicable to surface, saline, domestic, and industrial wastewater.

X1.1.10 *Trace Element Analysis of Industrial Furnace Feedstreams and Waste*—Practice D5513: This practice describes the multi-stage microwave digestion of typical industrial furnace feedstream materials using nitric, hydrofluoric, and boric acids for the subsequent determination of trace metals using atomic spectroscopy. The procedure is also effective for coal, and other waste materials such as fly ash, foundry sand, alum process residue, cement kiln dust, and so forth.

X1.1.11 *Lead Analysis in Paint Samples by Hotplate or Microwave Digestion*—Practice E1645: This practice describes the digestion procedures using a hot plate or microwave oven or apparatus for paint samples that are to be analyzed for their lead content. This practice is based on NIOSH Methods 7082 and 7105, and on an EPA standard operating procedure for lead in paint: NTIS No. PB92-114172. Lead is solubilized by digestion with nitric acid and hydrogen peroxide facilitated by microwave energy. The digested sample solution can be analyzed by AAS or ICP-AES for its lead content.

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